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[19] 中华人民共和国国家知识产权局

[51] Int. Cl.

C08G 65/48

## [12] 发明专利申请公开说明书

[21] 申请号 01136626.5

[43] 公开日 2002 年 4 月 17 日

[11] 公开号 CN 1344756A

[22] 申请日 2001.10.23 [21] 申请号 01136626.5

[71] 申请人 清华大学

地址 100084 北京市海淀区清华园

[72] 发明人 张 健 孙民伟

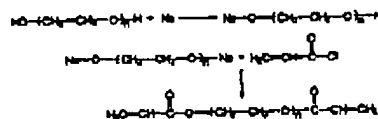
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权利要求书 1 页 说明书 4 页 附图页数 1 页

[54] 发明名称 一种交联剂及其高吸水性树脂的制备方法

[57] 摘要

一种交联剂及其高吸水性树脂的制备方法,先用分子量 200—1500 的聚乙二醇减压蒸馏,与金属钠粉反应得到聚乙二醇钠;再以氯仿为溶剂,将聚乙二醇钠与丙烯酸酐在一定条件下密闭反应,将反应物过滤、减压蒸馏得到不同分子量的交联剂二丙烯酸聚乙二醇。其后在单体丙烯酸中加入去离子水,用氢氧化钠部分中和,加入 2-甲基-(2-丙烯酸胺基)丙烷磺酸钠,通氮气,加入上述交联剂;最后再加入过氧化物引发剂进行反应,即可制得高吸水性树脂。本发明的交联剂,分子链长,活性适中;其高吸水性树脂交联均匀,线型可溶聚合物少,吸水速度快,吸盐倍数高,吸盐水达饱和时,水凝胶仍具有一定的强度。



知识产权出版社出版

ISSN 1008-4274

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## 权 利 要 求 书

1. 一种交联剂的制备方法, 该方法按如下步骤进行:

(1) 将分子量 200—1500 的一定量的聚乙二醇减压蒸馏除去水份, 与金属钠粉 按摩尔比 1:2—4 投料到反应器中, 磁力搅拌, 反应 1—3 小时, 分离得到聚乙二醇钠:

(2) 以氯仿为溶剂, 将聚乙二醇钠与丙烯酰氯按摩尔比 1:2—3 投放到反应器中, 磁力搅拌, 在 20—50℃ 的条件下密闭反应 4—8 小时;

(3) 将上述反应物过滤, 除去反应中生成的氯化钠, 再减压蒸馏除去未反应的丙烯酰氯和溶剂, 制得无色粘稠状液体, 即为不同分子量的交联剂二丙烯酸聚乙二醇酯。

2. 采用权利要求 1 所制交联剂的一种高吸水性树脂的制备方法, 该方法按如下步骤进行:

(1) 在单体丙烯酸中加入其体积 0.5—6 倍的去离子水, 用氢氧化钠部分中和成中和度为 40—80% 的丙烯酸溶液, 在部分中和的丙烯酸溶液中按 1:0—5 加入 2-甲基-(2-丙烯酰胺基) 丙烷磺酸钠, 通氮气, 氮气流量 15—50L/h, 搅拌均匀;

(2) 在上述反应溶液中再加入单体丙烯酸和 2-甲基-(2-丙烯酰胺基) 丙烷磺酸钠总摩尔数 0.02—0.5% 的不同分子量的交联剂二丙烯酸聚乙二醇酯, 搅拌均匀;

(3) 最后加入单体总质量 0.05—1% 的过氧化物引发剂, 搅拌均匀, 50—80℃ 条件下反应 0.5—2 小时, 将产物从反应器中取出, 100±5℃ 恒温 1—2 小时, 粉细得到高吸水性树脂。

3. 按照权利要求 2 所述的一种交联剂及其高吸水性树脂的制备方法, 其特征在于步骤

(3) 中的过氧化物引发剂可以是过硫酸钠、过硫酸钾、过硫酸铵、过氧化氢、叔丁基过氧化氢和异丙苯过氧化氢中的任意一种。

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## 说明书

## 一种交联剂及其高吸水性树脂的制备方法

## 技术领域:

本发明涉及一种交联剂及其利用该交联剂制备高吸水性树脂的方法,属于高分子材料技术领域。

## 背景技术:

高吸水性材料是一种能吸收自重几百至上千倍水的功能性高分子材料,最近二十年,取得了迅猛发展。其中,交联剂是制备高吸水性材料的重要组分,极大地影响着高吸水性材料的吸水性能。交联剂是含有两个或两个以上反应活性官能团的化合物,可以通过缩合或自由基聚合方式交联其它单体。目前使用的众多乙烯基交联剂,如(甲基)丙烯酸烯丙酯、聚乙烯(甲基)丙烯酸酯、N-甲基-N-乙烯基丙烯酰胺、对苯二乙烯、亚甲(乙)基双(甲基)丙烯酰胺、二(甲基)丙烯酸三羟甲基丙烷酯、N,N-二烯丙基丙烯酰胺、醋酸二烯丙基氧基酯、二(甲基)丙烯酸乙二醇酯、三烯丙基胺、三(甲基)丙烯酸三羟甲基丙烷酯、三(甲基)丙烯酸丙三醇酯、丙烯酸甲基丙烯酸丙三醇酯、膦酸三烯丙基酯、(磷酸)异膦酸三烯丙基酯、四烯丙氧基乙烷、四(甲基)丙烯酸季戊四醇酯及六(甲基)丙烯酸二季戊四醇酯等,这些交联剂的缺点是分子链短,反应活性很高,反应初期交联密度高,反应后期很少交联,主要生成线型可溶性聚合物,包覆聚合物凝胶,导致其吸水性能差。文献(D J Arriola, S S Cutié, D E Henton *et al.* Journal of Applied Polymer science, 1997, 63(4): 439)中公开了一种制备高吸水性树脂的方法,导致交联不均匀以及交联网格小,因此,难以获得吸水性能很好的高吸水性树脂。

使用目前常用的交联剂亚甲基-双丙烯酰胺,如JP 昭 60-161409 和 US4525527 中丙烯酸与丙烯酰胺二元共聚制备的高吸水性树脂,对蒸馏水和 1%氯化钠盐水的吸水倍率分别为 600—1300g/g 和 50—100g/g,反应时间需 4 小时以上;CN85103771 中采用淀粉接枝丙烯酸制备的高吸水性树脂最高能吸收自重 2000 倍左右的蒸馏水;Wen-Fu Lee 等(Journal of Applied Polymer Science, 1997, 64(9): 1701~1712)用丙烯酸与 3-二甲基-(2-甲基丙烯酰氧乙基)铵丙烷磺酸钠制备的高吸水性树脂在去离子水和 0.9%氯化钠盐水中的吸水倍率分别为 1435g/g 和 96g/g。

## 发明内容:

本发明的目的是提供一种交联剂及其利用该交联剂制备高吸水性树脂的方法,旨在制备分子链长度不同、反应活性适中的同系物交联剂,并用于高吸水性树脂的制备,以克服现有交联剂的不足,方便快捷地制备吸水性能好而且容易调控的高吸水性材料,以满足不同应

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用领域的需求。

本发明的一种交联剂及其高吸水性树脂的制备，其制备方法是首先制备不同分子量的交联剂二丙烯酸聚乙二醇酯，然后利用该交联剂高吸水性树脂，其具体方法按如下步骤进行：

- (1) 将分子量 200—1500 的一定量的聚乙二醇减压蒸馏除去水份，与金属钠粉按摩尔比 1:2—4 投料到反应器中，磁力搅拌，反应 1—3 小时，分离得到聚乙二醇钠；
- (2) 以氯仿为溶剂，将聚乙二醇钠与丙烯酰氯按摩尔比 1:2—3 投放到反应器中，磁力搅拌，在 20—50℃ 的条件下密闭反应 4—8 小时；
- (3) 将上述反应物过滤，除去反应中生成的氯化钠，再减压蒸馏除去未反应的丙烯酰氯和溶剂，制得无色粘稠状液体，即为不同分子量的交联剂二丙烯酸聚乙二醇酯。

利用所制的交联剂二丙烯酸聚乙二醇酯制备高吸水树脂的方法按如下步骤进行：

- (1) 在单体丙烯酸中加入其体积 0.5—6 倍的去离子水，用氢氧化钠部分中和成中和度为 40—80% 的丙烯酸溶液，在部分中和的丙烯酸溶液中按 1:0—5 加入 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠，通氮气，氮气流量 15—50L/h，搅拌均匀；
- (2) 在上述反应溶液中再加入单体丙烯酸和 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠总摩尔数 0.02—0.5% 的不同分子量的交联剂二丙烯酸聚乙二醇酯，搅拌均匀；
- (3) 最后加入单体总质量 0.05—1% 的过氧化物引发剂，搅拌均匀，50—80℃ 条件下反应 0.5—2 小时，将产物从反应器中取出，100±5℃ 恒温 1—2 小时，粉碎得到高吸水性树脂。

其中步骤(3)中的过氧化物引发剂可以是过硫酸钠、过硫酸钾、过硫酸铵、过氧化氢、叔丁基过氧化氢和异丙苯过氧化氢中的任意一种。

本发明的交联剂及其制备的高吸水性树脂，其优点在于：

- (1) 交联剂的原料丰富易得，制备方法简单易行，活性适中，储存方便。
- (2) 交联剂的分子链越长，高吸水性树脂的交联网络越大，容纳的水越多，因此高吸水性树脂的吸水倍率越高。
- (3) 高吸水性树脂交联均匀，线型可溶聚合物少，吸水速度快。
- (4) 高吸水性树脂在去离子水和 0.9% 氯化钠溶液中的吸水倍率分别为 1600—4010g/g 和 92—260g/g，可根据不同的吸水性能要求快速方便地制备期望的高吸水性树脂。
- (5) 高吸水性树脂的吸盐水倍率高，吸盐水达饱和时，水凝胶仍具有一定的强度。
- (6) 高吸水性树脂的制备可以在 2 小时以内完成，其反应时间短、收率高、易干燥和粉碎，有利于降低生产成本。

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附图说明:

图 1 是交联剂的合成路线示意图。

图 2 是高吸水性树脂在去离子水和 0.9%NaCl 中的吸水倍率与交联剂分子量之间的关系曲线图。

具体实施方式:

#### 1. 交联剂的制备

实施例 1:

将分子量 200 的聚乙二醇减压蒸馏除去水份, 与金属钠粉按摩尔比 1:2 投料到反应器中, 磁力搅拌, 反应 2 小时, 分离得到聚乙二醇钠。然后以氯仿为溶剂, 将聚乙二醇钠与丙烯酰氯按摩尔比 1:2.2 投放到反应器中, 磁力搅拌, 20℃密闭反应 4 小时, 过滤除去反应生成的氯化钠, 再减压蒸馏除去未反应的丙烯酰氯和溶剂, 制得无色粘稠状液体交联剂二丙烯酸聚乙二醇酯。

实施例 2:

将分子量 1000 的聚乙二醇减压蒸馏除去水份, 与金属钠粉按摩尔比 1:3 投料到反应器中, 磁力搅拌, 反应 2.5 小时, 分离得到聚乙二醇钠。然后以氯仿为溶剂, 将聚乙二醇钠与丙烯酰氯按摩尔比 1:2.6 投放到反应器中, 磁力搅拌, 30℃密闭反应 7 小时, 过滤除去反应生成的氯化钠, 再减压蒸馏除去未反应的丙烯酰氯和溶剂, 制得无色粘稠状液体交联剂二丙烯酸聚乙二醇酯。

实施例 3:

将分子量 1500 的聚乙二醇减压蒸馏除去水份, 与金属钠粉按摩尔比 1:2.5 投料到反应器中, 磁力搅拌, 反应 3 小时, 分离得到聚乙二醇钠。然后以氯仿为溶剂, 将聚乙二醇钠与丙烯酰氯按摩尔比 1:3 投放到反应器中, 磁力搅拌, 50℃密闭反应 8 小时, 过滤除去反应生成的氯化钠, 再减压蒸馏除去未反应的丙烯酰氯和溶剂, 制得无色粘稠状交联剂二丙烯酸聚乙二醇酯。

#### 2. 高吸水性树脂的制备

实施例 1:

在单体丙烯酸中加入其体积 0.5 倍的去离子水, 用氢氧化钠部分中和至中和度为 50% 的丙烯酸溶液, 在部分中和的丙烯酸溶液中按 1:0.1 加入 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠, 通氮气, 氮气流量 20L/h, 搅拌均匀, 再加入单体丙烯酸和 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠总摩尔数 0.3% 的交联剂二丙烯酸聚乙二醇酯(聚乙二醇分子量 1500), 搅拌均匀, 最后加入单体总质量 0.1% 的过硫酸铵, 搅拌均匀, 55℃反应 2 小时, 将产物从反应器中取出, 100±5℃恒温 1 小时, 粉细得到高吸水性树脂。用称重法测得在去离子水中的吸

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水倍率 3830g/g, 在 0.9%氯化钠盐水中的吸水倍率 106g/g.

#### 实施例 2:

在丙烯酸中加入其体积 1 倍的去离子水, 用氢氧化钠部分中和至中和度为 60%的丙烯酸溶液, 在部分中和的丙烯酸溶液中按 1:1 加入 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠, 通氮气, 氮气流量 15L/h, 搅拌均匀, 再加入单体丙烯酸和 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠总摩尔数 0.4%的交联剂二丙烯酸聚乙二醇酯(聚乙二醇分子量 1000), 搅拌均匀, 最后加入单体总质量 0.3%的过硫酸钾, 搅拌均匀, 60℃反应 1 小时, 将产物从反应器中取出, 100±5℃恒温 1.5 小时, 粉细得到高吸水性树脂. 用称重法测得在去离子水中的吸水倍率 3520g/g, 在 0.9%氯化钠盐水中的吸水倍率 260g/g.

#### 实施例 3:

在单体丙烯酸中加入其体积 3 倍的去离子水, 用氢氧化钠部分中和至中和度为 80%的丙烯酸溶液, 在部分中和的丙烯酸溶液中按 1:3 加入 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠, 通氮气, 氮气流量 30L/h, 搅拌均匀, 再加入单体丙烯酸和 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠总摩尔数 0.02%的交联剂二丙烯酸聚乙二醇酯(聚乙二醇分子量 200), 搅拌均匀, 最后加入单体总质量 0.5%的过硫酸钠, 搅拌均匀, 70℃反应 1 小时, 将产物从反应器中取出, 100±5℃恒温 2 小时, 粉细得到高吸水性树脂. 用称重法测得在去离子水中的吸水倍率 1600g/g, 在 0.9%氯化钠盐水中的吸水倍率 165g/g.

#### 实施例 4:

在丙烯酸中加入其体积 5 倍的去离子水, 用氢氧化钠部分中和至中和度为 80%的丙烯酸溶液, 在部分中和的丙烯酸溶液中按 1:5 加入 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠, 通氮气, 氮气流量 40L/h, 搅拌均匀, 再加入单体丙烯酸和 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠总摩尔数 0.06%的交联剂二丙烯酸聚乙二醇酯(聚乙二醇分子量 600), 搅拌均匀, 最后加入单体总质量 0.8%的过硫酸铵, 搅拌均匀, 80℃反应 40 分钟, 将产物从反应器中取出, 100±5℃恒温 2 小时, 粉细得到高吸水性树脂. 用称重法测得在去离子水中的吸水倍率 2480g/g, 在 0.9%氯化钠盐水中的吸水倍率 238g/g.

#### 实施例 5:

在单体丙烯酸中加入其体积 6 倍的去离子水, 用氢氧化钠部分中和至中和度为 70%的丙烯酸溶液, 通氮气, 氮气流量 15L/h, 搅拌均匀, 再加入单体丙烯酸和 2-甲基-(2-丙烯酰胺基)丙烷磺酸钠总摩尔数 0.05%的交联剂二丙烯酸聚乙二醇酯(聚乙二醇分子量 1400), 搅拌均匀, 最后加入单体总质量 0.4%的过硫酸钾, 搅拌均匀, 65℃反应 1.5 小时, 将产物从反应器中取出, 100±5℃恒温 1.5 小时, 粉细得到高吸水性树脂. 用称重法测得在去离子水中的吸水倍率 4010g/g, 在 0.9%氯化钠盐水中的吸水倍率 92g/g.

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## 说明书附图

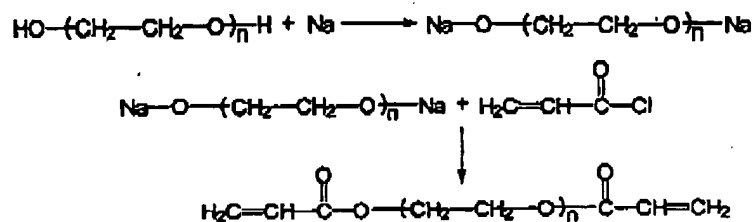


图 1

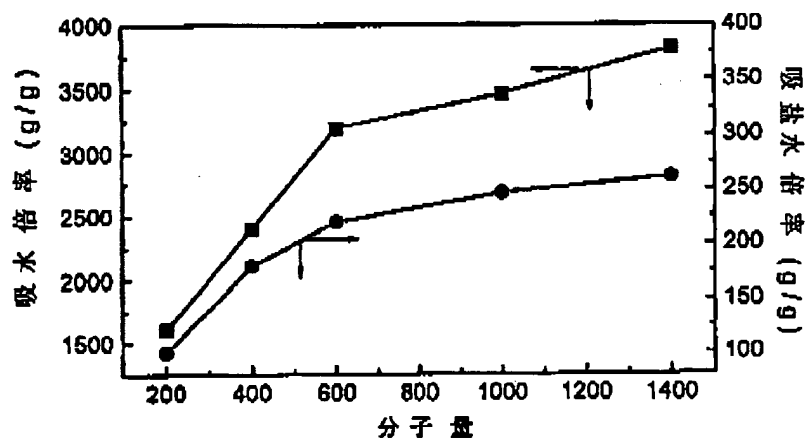


图 2

English translation of CN 1344756 A

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**Crosslinking agent and preparation of super absorbent resin**

**Abstract:** The present invention relates to a crosslinking agent and a method for preparing a super absorbent resin using the crosslinking agent. The preparation of a crosslinking agent comprises the following steps: distilling polyethylene glycol having a molecular weight of from 200 to 1500 under vacuum, then reacting with metal sodium powder to obtain poly(ethylene glycol) sodium; using chloroform as a solvent, and reacting poly(ethylene glycol) sodium with acryloyl chloride under certain conditions; and filtering the reaction mixture and distilling under vacuum to obtain a crosslinking agent of poly(ethylene glycol) diacrylate with a desired molecular weight. The method of preparing a super absorbent resin comprises the following steps: adding deionized water to acrylic acid monomer, partially neutralizing with sodium hydroxide, adding sodium 2-methyl-(2-acrylamido)propane-sulfonate, feeding nitrogen gas; adding to the reaction solution the crosslinking agent; and adding a peroxide initiator and reacting to obtain the super absorbent resin. The crosslinking agent of the present invention has a long molecular chain and a moderate activity. The super absorbent resin of the present application is homogeneously crosslinked, contains little linear soluble polymers, and has a high water absorption rate and a high water absorbency and a relatively high strength.



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What is claimed is:

1. A method for preparing a crosslinking agent, comprising the following steps:
  - (1) distilling a certain quantity of polyethylene glycol having a molecular weight of from 200 to 1500 under vacuum to remove water, adding the polyethylene glycol and metal sodium powder at mole ratio of 1 : 2-4 to a reactor, and reacting under magnetic stirring for 1-3 hours, and separating to obtain poly(ethylene glycol) sodium;
  - (2) using chloroform as a solvent, adding poly(ethylene glycol) sodium and acryloyl chloride at mole ratio of 1 : 2-3 to the reactor, and sealing the reactor and performing the reaction at 20-50°C for 4-8 hours under magnetically stirring; and
  - (3) filtrating the reaction mixture to remove sodium chloride produced during reaction, then removing unreacted acryloyl chloride and solvent via vacuum distillation to obtain a colorless viscous liquid, i.e., a crosslinking agent of poly(ethylene glycol) diacrylate with a desired molecular weight.
2. A method for preparing a super absorbent resin using the crosslinking agent prepared in claim 1, comprising the following steps:
  - (1) adding deionized water to acrylic acid monomer at volume ratio of 0.5-6 :1, partially neutralizing with sodium hydroxide to obtain an acrylic acid solution with a neutralization degree of 40-80%, adding sodium 2-methyl-(2-acrylamido)propane-sulfonate to the partially neutralized acrylic acid solution at ratio of 1 : 0-5, feeding nitrogen gas at a flux of 15-50 l/h, and stirring for uniformly mixing;
  - (2) adding to the reaction solution the crosslinking agent poly(ethylene glycol) diacrylate with a desired molecular weight and having an amount of 0.05-0.5% based on the total mole of acrylic acid monomers and

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2-methyl-(2-acrylamido)propane-sulfonate, and stirring for uniformly mixing;  
and

(3) adding a peroxide initiator having an amount 0.05-1% based on the total mass of monomers to the reactor, stirring for uniformly mixing, reacting at 50-80°C for 0.5-2 hours, taking out the reaction product from the reactor, and keeping at a temperature of  $100 \pm 5^\circ\text{C}$  for 1-2 hours, and pulverizing to obtain a fine super absorbent resin.

3. The method for preparing a super absorbent resin according to claim 2, wherein the peroxide initiator in step (3) is any one of sodium persulfate, potassium persulfate, ammonium persulfate, hydrogen peroxide, tert-butyl hydroperoxide and cumene hydroperoxide.

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**Crosslinking agent and preparation of super absorbent resin****Technical Field**

The present invention relates to a crosslinking agent and a method for preparing a super absorbent resin using the crosslinking agent, and belongs to the high molecular material field.

**Background Art**

Super absorbent resin is a functional high molecular material capable of absorbing water several hundreds to several thousands times higher than its weight. In recent twenty years, it has been developed rapidly. Crosslinking agent plays an important role in the preparation of high absorbent resin and greatly affects the performance of high absorbent resin. Crosslinking agent refers to a compound containing two or more reactively active functional groups and can crosslink other monomers by polycondensation or free-radical polymerization. At present, a plurality of vinyl crosslinking agents, e.g. propyl (meth)acrylate, polyethylene(meth)acrylate, N-methyl-N-vinyl-acrylate, p-divinyl benzene, N,N'-methylene-bis-(meth)acrylate, n,n'-ethylene-bis-(meth)acrylate, trimethylolpropane di(meth)acrylate, N,N-diallylacrylamide, diallyloxy acetate, glycol di(meth)acrylate, triallylamine, trimethylolpropane tri(meth)acrylate, glycerol tri(meth)acrylate, glycerol acrylate methacrylate, triallyl cyanurate, tetraallyloxyethane, pentaerythritol tetra(meth)acrylate, and dipentaerythritol hexa(meth)acrylate, etc., have a high reactive activity, cause a high crosslinking density at initial reaction phase and little crosslinking reaction at post reaction phase, and linear soluble polymers are mainly produced to cover polymeric gel, thereby resulting in a poor hydroscopicity. The reference (D.J. Arriola, S.S. Cutie, D.E. Henton et al, Journal of Applied Polymer Science, 1997, 63(4):139) disclosed a method for preparing a super absorbent resin, while non-homologous crosslinking reaction produced and small crosslinking meshes appeared, and a super

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absorbent resin with a good hydroscopicity was not obtained.

When the crosslinking agent N,N'-methylene-bis-acrylamide was used, for example, in JP80-161409 and US45425527, the super absorbent resin prepared by polymerizing acrylic acid and acrylamide for more than 4 hours has a water absorbency in distilled water or in 1% NaCl solution of 600-1300 g/g or 50-100 g/g, respectively; in CN85103771, the super absorbent resin prepared from starch grafted acrylic acid can absorb water 2000 times higher than its weight; in the reference (Wen-Fu Lee et al, Journal of Applied Polymer Science, 1997, 64(9): 1701-1712), the super absorbent resin prepared from acrylic acid and sodium 3-dimethyl-(2-methylacryloyloxyethyl)ammonium propane sulfonate has a water absorbency in distilled water or in 0.9% NaCl solution of 1435 g/g or 96 g/g, respectively.

#### Contents of the Invention

The object of the present invention is to provide a crosslinking agent and a method for preparing a super absorbent resin using the crosslinking agent. The present aims to prepare a series of crosslinking agents which have a different chain length and a suitable reactive activity and can be used to preparing super absorbent resin to overcome the disadvantages of the crosslinking agents in the prior art, and to prepare super absorbent resins which have a good water absorption performance and are easy to be controlled to meet the requirements in different fields.

In the invention, a crosslinking agent poly(ethylene glycol)diacrylate was prepared at first, then a super absorbent resin was prepared using the crosslinking agent.

The method for preparing the crosslinking agent comprises the following steps:

- (1) distilling removing a certain quantity of polyethylene glycol having a molecular weight of from 200 to 1500 under vacuum to remove water,

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adding the polyethylene glycol and metal sodium powder at mole ratio of 1 : 2-4 into a reactor, and reacting under magnetic stirring for 1-3 hours, and separating to obtain poly(ethylene glycol) sodium;

- (2) using chloroform as a solvent, adding poly(ethylene glycol) sodium and acryloyl chloride at mole ratio of 1 : 2-3 to the reactor, and sealing the reactor and performing the reaction at 20-50°C for 4-8 hours under magnetically stirring; and
- (3) filtrating the reaction mixture to remove sodium chloride produced during reaction, then removing unreacted acryloyl chloride and solvent via vacuum distillation to obtain a colorless viscous liquid, i.e., a crosslinking agent of poly(ethylene glycol) diacrylate with a desired molecular weight.

The method for preparing a super absorbent resin using the crosslinking agent prepared comprises the following steps:

- (1) adding deionized water to acrylic acid monomers, wherein the volume of deionized water is 0.5-6 times as that of acrylic acid monomer, partially neutralizing with sodium hydroxide to obtain an acrylic acid solution with a neutralization degree of 40-80%, adding sodium 2-methyl-(2-acrylamido)propane-sulfonate to the partially neutralized acrylic acid solution at ratio of 1 : 0-5, feeding nitrogen gas at a flux of 15-50 l/h, and stirring for uniformly mixing;
- (2) adding to the reaction solution the crosslinking agent poly(ethylene glycol)diacrylate with a desired molecular weight and having an amount of 0.05-0.5% based on the total mole of acrylic acid monomers and 2-methyl-(2-acrylamido)propane-sulfonate, and stirring for uniformly mixing; and
- (3) adding a peroxide initiator having an amount 0.05-1% based on the total mass of monomers to the reactor, stirring for uniformly mixing, reacting at 50-80°C for 0.5-2 hours, taking out the reaction product from the reactor,

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and keeping at a temperature of  $100\pm 5^{\circ}\text{C}$  for 1-2 hours, and pulverizing to obtain a fine super absorbent resin;

wherein the peroxide initiator in step (3) is any one of sodium persulfate, potassium persulfate, ammonium persulfate, hydrogen peroxide, tert-butyl hydroperoxide and cumene hydroperoxide.

The crosslinking agents and the super absorbent resins of the present application have the following advantages.

- (1) The raw materials for preparing the crosslinking agents are plentiful and easily available, the preparing method is simple and feasible, and the crosslinking agents per se have a moderate activity and are easy to be stored.
- (2) The crosslinking agents have a relatively longer chain; and the super absorbents have a bigger crosslinking meshes and a higher water absorption ratio.
- (3) The super absorbent resins are homogeneously crosslinked and contain little linear soluble polymers, so that they have a high water absorption rate.
- (4) The super absorbent resins have a water absorbency in distilled water or in 0.9% NaCl solution of 1600-4010 g/g or 92-260 g/g, respectively, and the desired super absorbent resins can be prepared rapidly and simply.
- (5) The super absorbent resins have a high water absorbency in salt solution, and the aqueous gels still possess certain strength when they arrive at saturated extent of adsorption in salt solution.
- (6) The preparation of the super absorbent resins may be completed within 2 hours, so that the reaction time is short and the yield is high. In addition, the super absorbent resins are easy to be dried and crushed, which benefits to lower the production cost.

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Description of drawings

Figure 1 is a schematic diagram of synthesis route of a crosslinking agent.

Figure 2 is a graph of the relationship between the water absorbency of a super absorbent resin in distilled water and 0.9% NaCl solution and the molecular weight of the crosslinking agent.

Examples

## 1. The preparation of crosslinking agents

## Example 1

Polyethylene glycol having a molecular weight of 200 was distilled under vacuum to remove water, then together with metal sodium powder at mole ratio of 1 : 2 were added to a reactor and a reaction were performed under magnetic stirring for 2 hours, and the reaction mixture was separated to obtain poly(ethylene glycol) sodium. Chloroform is used as a solvent, poly(ethylene glycol) sodium and acryloyl chloride at mole ratio of 1 : 2.2 were added to the reactor, then the reactor was sealed and a reaction were performed at 20°C for 4 hours under magnetic stirring. The final reaction mixture was filtered to remove sodium chloride produced during reaction, then unreacted acryloyl chloride and solvent was removed via vacuum distillation to obtain a colorless viscous liquid, i.e., a crosslinking agent of poly(ethylene glycol)diacrylate.

## Example 2:

Polyethylene glycol having a molecular weight of 1000 was distilled under vacuum to remove water, then together with metal sodium powder at mole ratio of 1 : 3 were added to a reactor and a reaction were performed under magnetic stirring for 2.5 hours, and the reaction mixture was separated to obtain poly(ethylene glycol) sodium. Chloroform is used as a solvent, poly(ethylene glycol) sodium and acryloyl chloride at mole ratio of 1 : 2.8 were added to the reactor, then the reactor was sealed and a reaction were

performed at 30°C for 7 hours under magnetic stirring. The final reaction mixture was filtered to remove sodium chloride produced during reaction, then unreacted acryloyl chloride and solvent was removed via vacuum distillation to obtain a colorless viscous liquid, i.e., a crosslinking agent of poly(ethylene glycol)diacrylate.

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#### Example 3:

Polyethylene glycol having a molecular weight of 1500 was distilled under vacuum to remove water, then together with metal sodium powder at mole ratio of 1 : 2.5 were added to a reactor and a reaction were performed under magnetic stirring for 3 hours, and the reaction mixture was separated to obtain poly(ethylene glycol) sodium. Chloroform is used as a solvent, poly(ethylene glycol) sodium and acryloyl chloride at mole ratio of 1 : 3 were added to the reactor, then the reactor was sealed and a reaction were performed at 50°C for 8 hours under magnetic stirring. The final reaction mixture was filtered to remove sodium chloride produced during reaction, then unreacted acryloyl chloride and solvent was removed via vacuum distillation to obtain a colorless viscous liquid, i.e., a crosslinking agent of poly(ethylene glycol)diacrylate.

#### 2. The preparation of super absorbent resins

##### Example 1:

Deionized water was added to acrylic acid monomer at a volume ratio of 0.5 : 1 to obtain a solution, then the solution was partially neutralized with sodium hydroxide to obtain an acrylic acid solution with a neutralization degree of 50%. Sodium 2-methyl-(2-acrylamido)propane-sulfonate was added to the partially neutralized acrylic acid solution at ratio of 1 : 0.1, and then nitrogen gas was fed at a flux of 20 l/h under stirring for uniformly mixing. The crosslinking agent poly(ethylene glycol)diacrylate (the molecular weight of polyethylene alcohol is 1500) having an amount of 0.3% based on the total mole of acrylic acid monomers and 2-methyl-(2-acrylamido)propane-sulfonate



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was added to the reaction solution under stirring for uniformly mixing, and then ammonium persulfate initiator having amount of 0.1% based on the total mass of monomers was added under stirring for uniformly mixing, and a reaction was performed at 55°C for 2 hours. The reaction mixture was taken out from the reactor, then hold at a temperature of 100±5°C for 1 hour, and pulverized to obtain a super absorbent resin. The water absorbency of the super absorbent resin in distilled water and 0.9% NaCl solution, measured by weighing method, is 3830 g/g or 106 g/g, respectively.

#### Example 2:

Deionized water was added to acrylic acid monomer at a volume ratio of 1 : 1 to obtain a solution, then the solution was partially neutralized with sodium hydroxide to obtain an acrylic acid solution with a neutralization degree of 60%. Sodium 2-methyl-(2-acrylamido)propane-sulfonate was added to the partially neutralized acrylic acid solution at ratio of 1 : 1, and then nitrogen gas was fed at a flux of 15 l/h under stirring for uniformly mixing. The crosslinking agent poly(ethylene glycol)diacrylate (the molecular weight of polyethylene alcohol is 1000) having an amount of 0.4% based on the total mole of acrylic acid monomers and 2-methyl-(2-acrylamido)propane-sulfonate was added to the reaction solution under stirring for uniformly mixing, and then ammonium persulfate initiator having amount of 0.3% based on the total mass of monomers was added under stirring for uniformly mixing, and a reaction was performed at 60°C for 1 hour. The reaction mixture was taken out from the reactor, then hold at a temperature of 100±5°C for 1.5 hours, and pulverized to obtain a super absorbent resin. The water absorbency of the super absorbent resin in distilled water and 0.9% NaCl solution, measured by weighing method, is 35200 g/g or 260 g/g, respectively.

#### Example 3:

Deionized water was added to acrylic acid monomer at a volume ratio of 1 :

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3 to obtain a solution, then the solution was partially neutralized with sodium hydroxide to obtain an acrylic acid solution with a neutralization degree of 80%. Sodium 2-methyl-(2-acrylamido)propane-sulfonate was added to the partially neutralized acrylic acid solution at ratio of 1 : 3, and then nitrogen gas was fed at a flux of 30 l/h under stirring for uniformly mixing. The crosslinking agent poly(ethylene glycol)diacrylate (the molecular weight of polyethylene alcohol is 200) having an amount of 0.02% based on the total mole of acrylic acid monomers and 2-methyl-(2-acrylamido)propane-sulfonate was added to the reaction solution under stirring for uniformly mixing, and then ammonium persulfate initiator having amount of 0.5% based on the total mass of monomers was added under stirring for uniformly mixing, and a reaction was performed at 70°C for 1 hour. The reaction mixture was taken out from the reactor, then hold at a temperature of 100±5°C for 2 hours, and pulverized to obtain a super absorbent resin. The water absorbency of the super absorbent resin in distilled water and 0.9% NaCl solution, measured by weighing method, is 1600 g/g or 165 g/g, respectively.

#### Example 4:

Deionized water was added to acrylic acid monomer at a volume ratio of 5 : 1 to obtain a solution, then the solution was partially neutralized with sodium hydroxide to obtain an acrylic acid solution with a neutralization degree of 80%. Sodium 2-methyl-(2-acrylamido)propane-sulfonate was added to the partially neutralized acrylic acid solution at ratio of 1 : 5, and then nitrogen gas was fed at a flux of 40 l/h under stirring for uniformly mixing. The crosslinking agent poly(ethylene glycol)diacrylate (the molecular weight of polyethylene alcohol is 600) having an amount of 0.06% based on the total mole of acrylic acid monomers and 2-methyl-(2-acrylamido)propane-sulfonate was added to the reaction solution under stirring for uniformly mixing, and then ammonium persulfate initiator having amount of 0.8% based on the total mass of monomers was added under stirring for uniformly mixing, and a reaction was

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performed at 80°C for 40 minutes. The reaction mixture was taken out from the reactor, then hold at a temperature of 100±5°C for 2 hours, and pulverized to obtain a super absorbent resin. The water absorbency of the super absorbent resin in distilled water and 0.9% NaCl solution, measured by weighing method, is 2480 g/g or 238 g/g, respectively.

**Example 5:**

Deionized water was added to acrylic acid monomer at a volume ratio of 6 : 1 to obtain a solution, then the solution was partially neutralized with sodium hydroxide to obtain an acrylic acid solution with a neutralization degree of 70%. Nitrogen gas was fed at a flux of 15 l/h under stirring for uniformly mixing. The crosslinking agent poly(ethylene glycol)diacrylate (the molecular weight of polyethylene alcohol is 1400) having an amount of 0.05% based on the total mole of acrylic acid monomers and 2-methyl-(2-acrylamido)propane-sulfonate was added to the reaction solution under stirring for uniformly mixing, and then ammonium persulfate initiator having amount of 0.4% based on the total mass of monomers was added under stirring for uniformly mixing, and a reaction was performed at 65°C for 1.5 hours. The reaction mixture was taken out from the reactor, then hold at a temperature of 100±5°C for 1.5 hour, and pulverized to obtain a super absorbent resin. The water absorbency of the super absorbent resin in distilled water and 0.9% NaCl solution, measured by weighing method, is 4010 g/g or 92 g/g, respectively.